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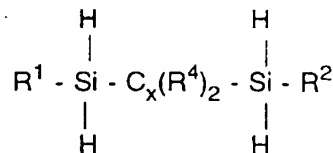
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(54) **Low temperature deposition of silicon dioxide using organosilanes**

(57) The present invention is a process for very low temperature chemical vapor deposition of silicon dioxide, comprising the steps of

a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;

b) introducing into said vacuum an organosilane containing feed and an oxygen containing feed, said organosilane containing feed consisting essentially of one or more compounds having the general formula:



wherein R¹ and R² are independently H, alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, but only one of R¹ and R² can be H, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6, and R⁴ is independently H, C_yH_{2y+1} where y = 1-6; and

c) maintaining said temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

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D cription

FIELD OF THE INVENTION

5 The present invention is directed to a low temperature deposition of silicon dioxide films on various substrates, such as semiconductor materials, using organosilanes, preferably organo bis (secondary silyls).

BACKGROUND OF THE INVENTION

10 In the fabrication of semiconductor devices, a thin passive layer of a chemically inert dielectric material such as, silicon dioxide (SiO_2) is essential. Thin layers of silicon dioxide function as a intermetallic dielectric material or as a passivation layer. Silicon dioxide coatings in the fabrication of semiconductor devices have a variety of applications. Some of these uses are; insulators between polysilicon and metal layers, between metal layers in multilevel metal systems, as getters, as diffusion sources, as diffusion and implantation masks, as capping layers and as passivation layers. See HANDBOOK OF THIN FILM TECHNOLOGY, Maissell, Leon I. and Glang, Reinhard, editors, Mc Graw Hill Book Company, New York, 1970, and SILICON PROCESSING FOR THE VLSI ERA, Wolf, Stanley, and Talbert, Richard N., editors, Lattice Press, Sunset Beach, California, 1986.

15 Deposition of silicon dioxide over large numbers of wafers can be accomplished using many precursors. Barry Gelernt, Semiconductor International March 1990. To date, there are three temperature zones at which thermal CVD silicon dioxide may be deposited. These are: Low temperature deposition, which is approximately $<450^\circ\text{C}$, medium temperature deposition which is at least 450°C , more preferably approximately $650\text{-}750^\circ\text{C}$ and high temperature deposition which is greater than 750°C , more preferably approximately 900°C or greater.

There are very few precursors which are known to deposit in the low temperature region.

25 1) 1,4-disilabutane (containing the group $-\text{SiH}_3$) is reported to deposit at temperatures as low as 100°C . One major drawback with 1,4-disilabutane is its safety. It is extremely flammable and due to its very high flammability, safe manufacture of 1,4-disilabutane is found to be difficult. A. K. Hochberg and D. A. Roberts Mat. Res. Soc. Symp. Proc. Vol 282, pp569, 1993 Material Research Society.

30 2) The LPCVD silane/oxygen process requires deposition temperatures from 350 to 450°C . In a LPCVD process deposition under 350°C does not occur. Under APCVD conditions silicon dioxide has been reported to deposit below 250°C using very dilute mixtures for small wafer loads, but the films are of poor quality. The major disadvantage is that silane is a pyrophoric, toxic compressed gas. Bennett, B.R., et al. US Patent # 4900591. Bennett, B. R et al. Appl. Phys. Lett. 50(4), pp197, 1987.

35 3) Diethylsilane and other ethylsilanes. A series of homologous ethylsilanes were studied as low temperature silicon dioxide precursors. Diethylsilane gave the best results as a medium temperature silicon dioxide deposition precursor. Diethylsilane pyrolyzes at 260°C , no deposition occurs below 340°C . Abrupt cessation of deposition rate is observed at pressures below 350mTorr and 340°C . A. K. Hochberg and D. L. O'Meara, J. Electrochem. Soc., Vol 136, pp1843, 1989.

40 4) Silacyclobutane deposited silicon dioxide as low as 350°C . This precursor is not stable and decomposes to a polymer at room temperature on standing for prolonged lengths of time. Silacyclopentane on the other hand does not deposit silicon dioxide below 360°C .

45 5) Other precursors which are listed in Table 1., Methyl propylsilane and Di-t-butylsilane deposit silicon dioxide at 480°C and 350°C respectively.

50 6) Dichlorosilane is reported to deposit silicon dioxide at much higher temperatures $550\text{-}900^\circ\text{C}$. The films are usually contaminated with particulates at lower temperatures. The precursor itself is a corrosive, toxic, pyrophoric compressed gas. SILICON PROCESSING FOR THE VLSI ERA, Volume 1, Wolf, Stanley and Tauber, Richard N., editors, Lattice Press, Sunset Beach, California. 1986, pp184; Chapple-Sokol J. D, Gordon R. G. Thin Solid Films 171, 291(1989).

55 The prior art has attempted to provide precursors which can deposit silicon dioxide at low temperatures below 450°C under appropriate conditions. Among these different source materials only silane and 1,4 disilabutane deposit silicon dioxide at temperatures below 400°C . However these precursors are extremely hazardous to handle or manufacture in large quantities. Silane is a pyrophoric compressed gas and 1,4 disilabutane is an extremely flammable liquid

and difficult to manufacture safely. With silane, rates of deposition and step coverage are poorer as the temperatures are reduced below 350°C. These and other problems in the prior art are overcome by the present invention, as will be set forth in greater detail below.

At higher pressures, depositions occur before reaching the wafers and homogeneous processes occur (powder formation). The major disadvantage is that silane is a pyrophoric, toxic, compressed gas.

As the deposition temperature is reduced below 350°C, there are very few stable and safe precursors. Prior to the present invention, only 1,4-disilabutane (a primary alkyldisilane, containing the group -SiH₃) is reported to deposit at temperatures below 350°C. One major drawback with 1,4-disilabutane is its safety. 1,4-disilabutane is highly reactive with oxygen and is extremely flammable. Due to its very high flammability, safe manufacture of 1,4-disilabutane is difficult.

Generally, reactivity of alkylsilanes with oxygen under elevated temperatures decreases in the order of primary (H₃SiR) > secondary (H₂SiR₂) > tertiary (HSiR₃) > quaternary (SiR₄).

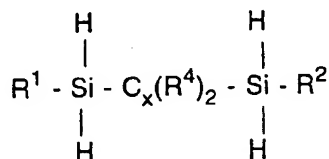
A large variety of "thin films" are used in the fabrication of Very Large Scale Integration (VLSI) devices. These deposited thin films can be of metals, semiconductors, or insulators. The films may be thermally grown or deposited from the vapor phase using low pressure chemical vapor deposition (LPCVD, see below).

In VLSI fabrication a large set of rigorous chemical, structural, process and electrical requirements should be satisfied. Purity of the film, thickness, uniformity and deposition rates are some of the strictly controlled parameters to facilitate fabrication of submicron features in a device. It is a major advantage in the fabrication and performance of the device if the deposition process can be carried out at temperatures lower than 350°C. Silicon source materials for depositing silicon dioxide under LPCVD conditions at these temperatures are limited to silane and diethylsilane. A safe, reliable low temperature silicon dioxide source material has applications in other technologies such as flat panel display devices or compound semiconductor device fabrication.

BRIEF SUMMARY OF THE INVENTION

The present invention is a process for low temperature chemical vapor deposition of silicon dioxide, comprising the steps of:

- a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;
- b) introducing into the vacuum a organosilane containing feed and an oxygen containing feed, the organosilane containing feed consisting essentially of one or more compounds having the general formula:



- wherein R¹ and R² are independently H, alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, but only one of R¹ and R² can be H, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6, and R⁴ is independently H, C_yH_{2y+1} where y = 1-6; and
- c) maintaining the temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

Preferably, the oxygen containing feed is selected from the group consisting of oxygen gas, N₂O, O₃ and mixtures thereof.

Preferably, the oxygen containing feed to organosilane containing feed ratio is between 0.5:1 and 10:1.

Preferably, the substrate is a silicon wafer.

Preferably, the organosilane is 1,2 bis(methylsilyl)ethane.

Preferably, the organosilane is 1-methylsilyl, 2-silyl ethane.

Preferably, R¹ and R² are independently alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6.

Preferably the present invention is a process for low temperature chemical vapor deposition of silicon dioxide, comprising the steps of:

- a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;
- b) introducing into the vacuum a 1,2 bis(methylsilyl)ethane containing feed and an oxygen containing feed; and

c) maintaining the temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

BRIEF DESCRIPTION OF THE DRAWING

FIG 1 is an FT-IR spectrum of a typical film of SiO_2 produced by the present invention's process using 1,2 bis (methylsilyl)ethane in which Transmittance is graphed against Wavenumbers (cm^{-1}).

DETAILED DESCRIPTION OF THE INVENTION

The present invention describes deposition of silicon dioxide at an unusually low temperature using organosilanes, such as organo bis (secondary silyls). These precursors are highly volatile, thermally stable and less hazardous than silane which is typically used for silicon dioxide deposition.

Economically, the largest industrial application of this invention is in the manufacture of integrated circuits in which silicon dioxide is deposited on a substrate comprising silicon or another layer in the composite construction of an integrated circuit; however, this invention is applicable to deposition of silicon dioxide on other substrates in the temperature range of 150 to 500°C, particularly using low pressure chemical vapor deposition.

Low pressure chemical vapor deposition processes (LPCVD) involve chemical reactions that are allowed to take place in the pressure range of 150 mtorr to 2 torr. Chemical Vapor Deposition (CVD) processes can be described in the following sequence of steps at a given temperature, pressure and ratio of the reactants:

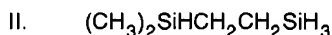
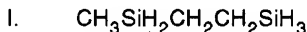
- 1) Reactants are introduced into the reaction chamber and may be diluted with inert gases, if needed.
 - 2) The reactants are allowed to diffuse to the substrate.
 - 3) The reactants are adsorbed on the substrate and the adsorbed molecules undergo migration.
 - 4) Chemical reactions occur on the surface and the gaseous byproducts of the reaction are desorbed leaving behind the deposited film.
- The reactions are initiated by several methods; e.g., thermal or photons.
Thermal energy is used in the LPCVD process, which occurs in a special reactor.

Horizontal and vertical tube hot wall reactors are the most widely used for LPCVD in VLSI manufacturing. They are employed for depositing poly-Si, silicon nitride and undoped and doped silicon dioxide films. These reactors are used extensively because they are economical, have high throughputs, the deposited films are uniform and can accommodate large diameter wafers (6" and 8"). Their main disadvantages are susceptibility to particulate contamination and low deposition rates.

The vacuum system consists of a rotary vane pump/roots blower combination and various cold traps. The reactor pressure is controlled by a capacitance manometer feedback to a throttle valve controller. Reactor loading consists of eighty 100 mm diameter silicon wafers at 9mm spacing in standard diffusion boats. The boats are positioned on a sled, so that the wafers centers are slightly above the center of the reaction tube. This produces a uniform conductance around the wafer peripheries by compensating for conductance restrictions caused by the boats and the sled. The temperature uniformity across the wafer load for the data presented is $\pm 1^\circ\text{C}$ as measured by an internal multi-junction thermocouple. Deposition uniformity down the wafer load is improved by a temperature ramp.

The deposition experiments of the present invention were carried out in a horizontal tube reactor, but the deposition with these precursors will occur even in a vertical tube reactor. The precursor was fed through an open injector to the first wafer position. Oxygen was also fed from the door of the furnace separately.

The secondary organosilane compounds of the present invention possess low flammability and low deposition temperature characteristics for silicon dioxide film formation. This compares favorably to 1,4-disilabutane, which is a primary alkylsilane. In order to reduce the flammability of 1,4-disilabutane, but to retain the low temperature deposition properties of the 1,4-disilabutane, several derivatives of 1,4-disilabutane were synthesized and investigated, two of the alkyl derivatives are listed below.



In addition to these compounds where there is at least one primary silane ($-\text{SiH}_3$), we have also investigated a series of secondary monosilanes (containing the group $-\text{SiH}_2$) such as diethylsilane, di (t-butyl)silane, methylpropylsilane, silacyclobutane, silacyclopentane and dichlorosilane.

Although these compounds showed promise in depositing at moderately low temperatures, compound I was still highly flammable. Compound II and the secondary monosilanes needed higher deposition temperatures. Deposition temperatures for the monosilanes are listed in Table 1.

We have discovered that 1,2 bis(methylsilyl)ethane, $\text{CH}_3\text{SiH}_2\text{CH}_2\text{CH}_2\text{SiH}_2\text{CH}_3$, a class of organo bis (secondary silyls) has the property to deposit silicon dioxide at very low temperatures. Our deposition results at 150°C are very surprising because other analogous secondary monosilane precursors such as diethylsilane, di (t-butyl)silane, methylpropylsilane, silacyclobutane, silacyclopentane and dichlorosilane do not deposit at such low temperatures. Although not wishing to be held to any particular theory, the low deposition temperature of the present invention is apparently due to the presence of two silicon atoms in the organosilane which are in close proximity.

Among secondary monosilane precursors, diethylsilane has been most extensively studied. Diethylsilane pyrolyzes at 260°C , no deposition occurs below 340°C . On the other hand, abrupt cessation of deposition rate is observed at pressures below 350mTorr and 340°C .

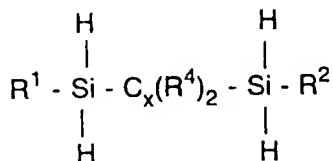
When we substituted 1, 2 bis(methylsilyl)ethane for diethylsilane, deposition of silicon dioxide was achieved even below 340°C . High deposition rates were obtained at pressures below 350mTorr and deposition temperatures as low as 150°C .

When compared to other analogous secondary monosilanes, the temperature of deposition using the organo bis (secondary silyls) of the present invention is much lower. High quality films over large numbers of wafers may be obtained under the conditions described in the experiments below. A comparison of deposition temperatures for a variety of secondary monosilanes and 1,2 bis (methylsilyl)ethane (an organo bis (secondary silyl)) are given in Table 1.

TABLE 1

Precursor	Deposition temperature ($^\circ\text{C}$)
Dichlorosilane	550
Methyl propylsilane	480
Di-t-butylsilane	350
Diethylsilane	340
1,1 Dimethyl 1,4 disilabutane	240
Silacyclopentane	360
Silacyclobutane	350
1,2 bis(methylsilyl)ethane	150

The organosilanes of the present invention comprise one or more compounds having the general formula:



wherein R^1 and R^2 are independently H, alkyl, alkenyl, alkynyl, or aryl, having C_1 to C_6 , but only one of R^1 and R^2 can be H, or R^1 and R^2 can be connected by an alkyl chain $\text{C}_x(\text{R}^3)_2$, where R^3 is independently H, $\text{C}_x\text{H}_{2x+1}$ and $x = 1-6$, and R^4 is independently H, $\text{C}_y\text{H}_{2y+1}$ where $y = 1-6$. Preferably, the organosilanes have only secondary silanes where R^1 and R^2 are independently alkyl, alkenyl, alkynyl, or aryl, having C_1 to C_6 , or R^1 and R^2 can be connected by an alkyl chain $\text{C}_x(\text{R}^3)_2$, where R^3 is independently H, $\text{C}_x\text{H}_{2x+1}$ and $x = 1-6$. Other organosilanes of the organo bis (secondary silyls) other than 1,2 bis(methylsilyl)ethane are contemplated by the present invention. Such compounds include 1,2 bis(ethylsilyl)ethane, 1,2 bis(propylsilyl)ethane, 1,3 bis(methylsilyl)propane, 1,3 bis(ethylsilyl)propane, and 1,3 bis(propylsilyl)propane. Cyclic organo bis (secondary silyls) are also contemplated, such as 1,4 silacyclohexane. Other organosilanes having at least one secondary silane are also contemplated, such as; 1-methylsilyl, 2-silyl ethane, 1-ethylsilyl, 2-silyl ethane, 1-propylsilyl, 2-silyl ethane, 1-methylsilyl, 3-silyl propane, 1-ethylsilyl, 3-silyl propane, 1-methylsilyl, 4-silyl butane.

The secondary organosilanes of the present invention and oxygen are allowed to react in the reactor tube at an elevated temperature. Reaction may occur either on the surface or very close to the wafer surface to deposit a thin silicon dioxide film. If the reaction occurs in the gas phase (a homogeneous reaction) then clusters of silicon dioxide are formed. When the reaction occurs close to the wafer surface then the resulting films are of good quality. Thus, one important requirement for CVD application is the degree to which heterogeneous reactions are favored over gas phase reactions. The CVD process can be grouped into a) gas-phase process and b) a surface process. The gas phase phenomenon is the rate at which gases impinge on the substrate. This is modeled by the rate at which gases cross the boundary layer that separates the bulk regions of flowing gas and substrate surface. Such transport processes occur by gas-phase diffusion, which is proportional to the diffusivity of the gas and concentration gradient across the

boundary layer. Several surface processes can be important when the gases reach the hot surface, but the surface reaction, in general, can be modeled by a thermally activated phenomenon which proceeds at a rate which is a function of the frequency factor, the activation energy, and the temperature. The surface reaction rate increases with increasing temperature. For a given surface reaction, the temperature may rise high enough so that the reaction rate exceeds the rate at which reactant species arrive at the surface. In such cases, the reaction cannot proceed any more rapidly than the rate at which reactant gases are supplied to the substrate by mass transport. This is referred to as a mass-transport limited deposition process. At lower temperatures, the surface reaction rate is reduced, and eventually the concentration of reactants exceeds the rate at which they are consumed by the surface reaction process. Under such conditions the deposition rate is reaction rate limited. Thus, at high temperatures, the deposition is usually mass-transport limited, while at lower temperatures it is surface-reaction rate-limited. In actual processes, the temperature at which the deposition condition moves from one of these growth regimes to the other is dependent on the activation energy of the reaction, and the gas flow conditions in the reactor. Thus, it is difficult to extrapolate process conditions or results from one pressure regime or temperature regime to another.

In processes that are run under reaction rate-limited conditions, the temperature of the process is an important parameter. That is, uniform deposition rates throughout a reactor require conditions that maintain a constant reaction rate. This, in turn, implies that a constant temperature must exist everywhere on all wafer surfaces. On the other hand, under such conditions, the rate at which reactants reach the surface is not important, since their concentration does not limit the growth rate. Thus, it is not as critical that a reactor be designed to supply an equal flux of reactants to all locations of a wafer surface. It will be seen that in low-pressure CVD LPCVD reactors, wafers can be stacked vertically and at very close spacing because such systems operate in a reaction rate limited mode. The reason for this is as follows: Under the low pressure of an LPCVD reactor at ~ 1 torr, the diffusivity of the gas species is increased by a factor of 1000 over that at atmospheric pressure, and this is only partially offset by the fact that the boundary layer, the distance across which the reactants must diffuse, increases by less than the square root of the pressure. The net effect is that there is more than an order of magnitude increase in the transport of reactants to and by-products away from the substrate surface, and the rate-limiting step is thus the surface reaction.

The present invention is a method of depositing substantially pure silicon dioxide films on silicon wafers by using secondary organosilane precursors, such as organo bis secondary silyls. The secondary organosilane sources have at least one secondary silane and preferably have two secondary silanes. These secondary silanes are non-pyrophoric, volatile liquids, which are safer to handle than silane. The deposition process is carried out at approximately 150mtorr-750mtorr in the temperature range of approximately 150°C to 500°C using vapors from the secondary organodisilane and oxygen. Optionally an inert gas diluent, such as nitrogen or argon, is used to dilute and control the rate of reaction. The molar feed ratio of the secondary organodisilane to oxygen is within the range of 0.5:1 to 0.5:50. Their use in chemical vapor deposition of silicon oxide layers on semiconductor substrates is comparable to the utilization of the primary organodisilanes of US Patent 5,204,141, which is hereby incorporated by reference herein in its entirety.

Example 1

The process involves reaction of 1,2 bis (methylsilyl)ethane with oxygen under LPCVD conditions. The precursor and oxygen are introduced into the heated reactor (150 to 500°C) via injectors placed at the door. The reactants are flowed over wafers into the evacuated chamber. The oxygen to silicon source was varied from 0.5:1 to 4:1 in different runs of the experiment. A continuous film of silicon dioxide is deposited upon the surface of a silicon wafer. These films are suitable for integrated circuit manufacture. A typical run was carried out in a 150mm hot wall LPCVD horizontal tube reactor, although the apparatus configuration is not critical. The process involves loading the quartz reactor with 75 to 100 silicon wafers, evacuating the system and then letting the wafers come to a desired temperature at which the deposition will be carried out. The energy required for this reaction can be supplied by either a plasma or simple resistive heating. However, simple, resistive heating is advantageous because the equipment is less expensive than that required for plasma type reactions and avoids radiative film damage often associated with plasma reactors.

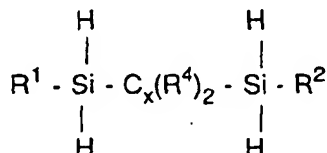
The films are characterized by infrared spectroscopy and refractive index. An FT-IR spectrum of a typical film is shown in FIG 1. The spectrum is consistent with silicon dioxide films deposited from other known oxide precursors e. g. diethylsilane. There are no strong absorptions in the Si-H stretching region or in the 3200cm^{-1} region where C-H stretching are observed. Refractive indices for these films were measured by ellipsometry at 632.4 nm . A mean value of 1.46 was obtained for films.

The primary industrial application of this invention is in the manufacture of semiconductor devices; however, the invention is applicable to any thin film deposition of SiO_2 on substrates which are capable of being heated to 150 to 500°C . The present invention has been set forth with regard to one or more specific embodiments, however the scope of the invention should be ascertained from the claims which follow.

Claims

1. A process for very low temperature chemical vapor deposition of silicon dioxide, comprising the steps of

a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;
 b) introducing into said vacuum an organosilane containing feed and an oxygen containing feed, said organosilane containing feed consisting essentially of one or more compounds having the general formula:



wherein R¹ and R² are independently H, alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, but only one of R¹ and R² can be H, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6, and R⁴ is independently H, C_yH_{2y+1} where y = 1-6; and

c) maintaining said temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

2. A process according to Claim 1 wherein the said oxygen containing feed is selected from the group consisting of oxygen gas, N₂O, O₃ and mixtures thereof.

3. A process according to Claim 1 wherein an oxygen containing feed to organosilane containing feed ratio is between 0.5:1 and 10:1.

4. A process according to Claim 1 wherein said substrate is a silicon wafer.

5. A process according to Claim 1 wherein said organosilane is 1,2 bis(methylsilyl)ethane.

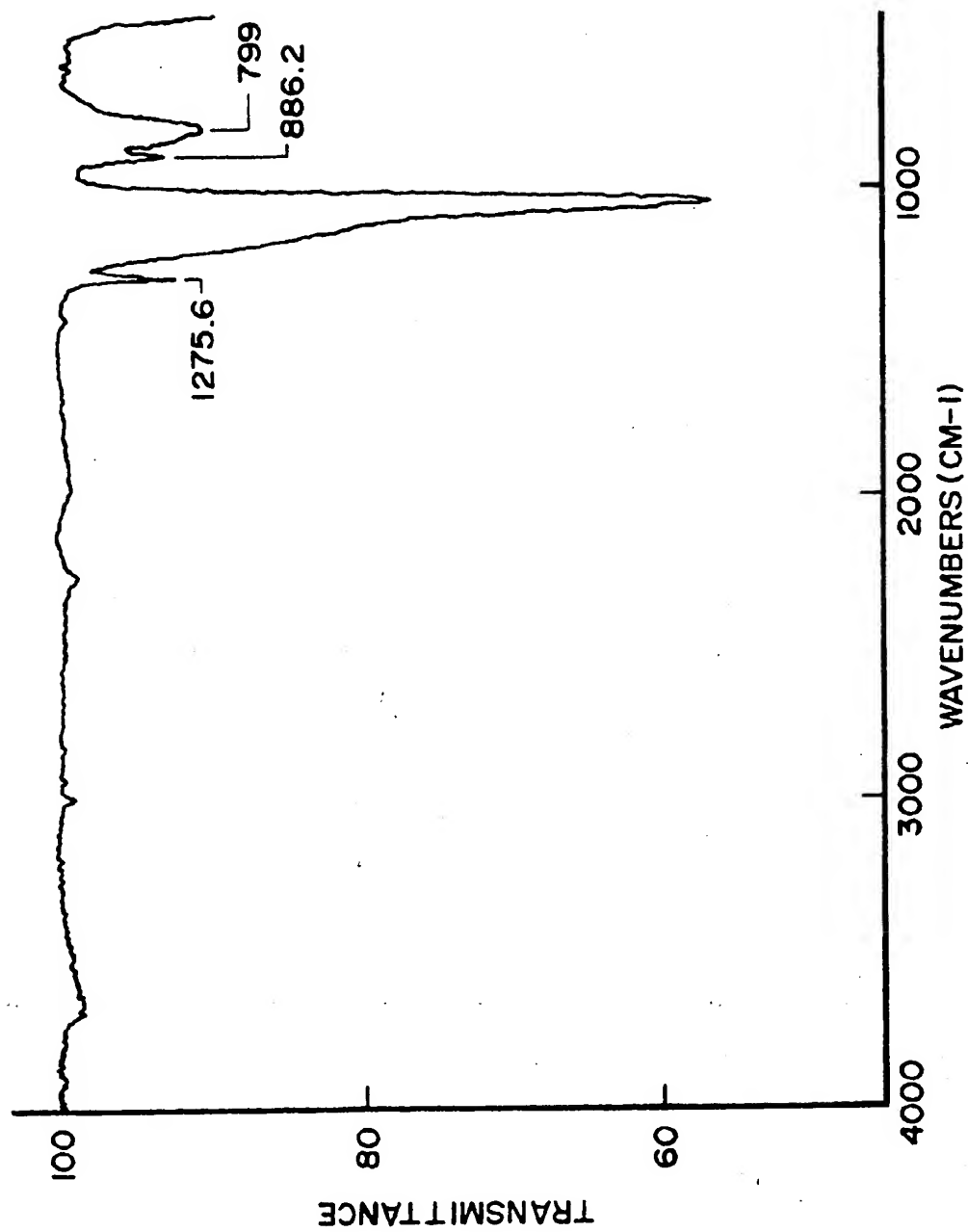
6. A process according to Claim 1 wherein said organosilane is 1-methylsilyl, 2-silyl ethane.

7. A process according to Claim 1 wherein R¹ and R² are independently alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6.

8. A process for low temperature chemical vapor deposition of silicon dioxide, comprising the steps of:

a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;
 b) introducing into the vacuum a 1,2 bis(methylsilyl)ethane containing feed and an oxygen containing feed; and
 c) maintaining the temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

FIG. 1



(19)



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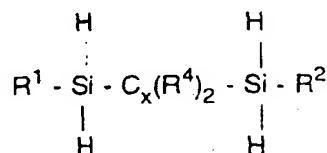
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(54) **Low temperature deposition of silicon dioxide using organosilanes**

(57) The present invention is a process for very low temperature chemical vapor deposition of silicon dioxide, comprising the steps of

a) heating a substrate upon which silicon dioxide is to be deposited to a temperature in the range of approximately 150 to 500°C in a vacuum maintained at a pressure in the range of approximately 50 to 750mTorr;

b) introducing into said vacuum an organosilane containing feed and an oxygen containing feed, said organosilane containing feed consisting essentially of one or more compounds having the general formula:



wherein R¹ and R² are independently H, alkyl, alkenyl, alkynyl, or aryl, having C₁ to C₆, but only one of R¹ and R² can be H, or R¹ and R² can be connected by an alkyl chain C_x(R³)₂, where R³ is independently H, C_xH_{2x+1} and x = 1-6, and R⁴ is independently H, C_yH_{2y+1} where y = 1-6; and

c) maintaining said temperature and vacuum thereby causing a thin film of silicon dioxide to deposit on the substrate.

EP 0 721 019 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 10 0018

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 387 403 A (AIR PROD & CHEM) 19 September 1990 * page 10, line 20 - page 13, line 20; claims 1-10 *	1-3,8	H01L21/316 H01L21/768
A	EP 0 533 129 A (AIR PROD & CHEM) 24 March 1993 * page 5, line 25 - page 8, line 28; claims 1-22 *	1-4,8	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16 April 1997	Examiner Königstein, C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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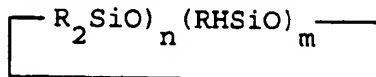
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Sevenoaks, Kent TN13 1XR (GB)(54) **Water-repellent thin films and methods for the preparation thereof**

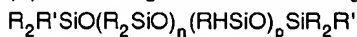
(57) There is disclosed a hard, water-repellent thin film which is obtained by plasma polymerizing an SiH-containing organosiloxane on a substrate, wherein the organosiloxane is selected from

(A) a cyclic organosiloxane of the general formula



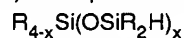
wherein R denotes a monovalent hydrocarbon radical having 1 to 18 carbon atoms, n is an integer having a value of zero or greater and m is an integer having a value of 3 to 20;

(B) a linear organosiloxane of the general formula



wherein R and n are as defined above, R' is selected from a monovalent hydrocarbon radical having 1 to 18 carbon atoms or a silicon-bonded hydrogen atom and p is an integer having a value of 1 to 20, with the proviso that organosiloxane (B) contains at least 3 silicon-bonded hydrogen atoms; or

(C) a compound of the general formula



wherein R is as defined above and x is 3 or 4.

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Description

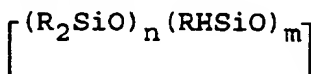
The present invention relates to water-repellent thin films obtained by the plasma polymerization of SiH-containing organosiloxane and to a method for preparing same.

Dimethylpolysiloxanes exhibit low surface tensions of 20 to 22 mN/m and, as a consequence, are used as treatment agents for making various types of substrates water repellent. However, these water-repellent coatings are generally soft, which can prevent their use depending on the particular application. It is also known that highly water-repellent substrates are obtained by dissolving SiH-containing methylhydrogenpolysiloxane in organic solvent, coating this solution on any of a variety of substrates, and drying by heating. Unfortunately, the formation of a uniform coating with this latter method is quite problematic. In addition, JP-A 63-67566 proposes a method for preparing spherical, polysiloxane-coated silica-gel powder that is highly suited for use as a gas chromatographic packing. In this method, a mixture of methylhydrogenpolysiloxane and spherical, silica-gel powder is exposed to a plasma. Again, however, it is quite difficult to obtain a uniform, homogeneous water-repellent thin film using this method.

The present invention takes as an object the introduction of water-repellent thin films that are both very hard and highly water repellent as evidenced by a large contact angle versus water. An additional object of this invention is the introduction of a method for preparing the described films.

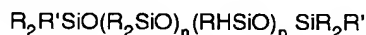
The present invention, therefore, is a water-repellent thin film obtained by the plasma polymerization on the surface of a substrate of an SiH-containing organosiloxane selected from the group consisting of:

(A) a cyclic organosiloxane with the general formula



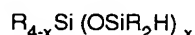
wherein R denotes a C_1 to C_{18} monovalent hydrocarbon radical, n is an integer with a value of zero or greater, and m is an integer with a value from 3 to 20;

(B) a linear organosiloxane with the general formula



wherein R denotes a C_1 to C_{18} monovalent hydrocarbon radical, R' is a C_1 to C_{18} monovalent hydrocarbon radical or a silicon-bonded hydrogen atom, n is an integer with a value of zero or greater, and p is an integer with a value from 1 to 20, with the proviso that this organosiloxane contains at least 3 silicon-bonded hydrogen atoms, and

(C) an organosiloxane with the general formula

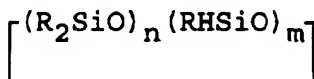


wherein R denotes a C_1 to C_{18} monovalent hydrocarbon radical and x is 3 or 4.

The present invention further relates to a method for the preparation of water-repellent thin films characterized in that an SiH-containing organosiloxane, as described above, is introduced into a plasma polymerization device and said SiH-containing organopolysiloxane is plasma polymerized in the presence of an oxygen-containing compound selected from the group consisting of water, air, and C_1 to C_{10} alcohols and thereby deposited on the surface of an inorganic or organic substrate.

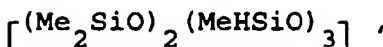
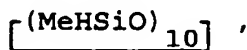
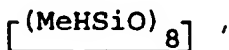
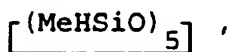
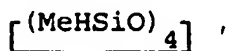
The water-repellent thin films of the present invention will be considered in detail. These water-repellent thin films are formed by the SiH-containing organosiloxane used by the present invention, which must contain at least 3 silicon-bonded hydrogen atoms in each molecule. This component is selected from the three types of organosiloxanes described above.

The first of these is (A) a cyclic organosiloxane with the following general formula:

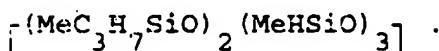


wherein R denotes a C_1 to C_{18} monovalent hydrocarbon radical and is exemplified by alkyl radicals such as methyl, ethyl, propyl, butyl, and pentyl; aryl radicals such as phenyl, tolyl, and xylyl; aralkyl radicals such as benzyl, and phenethyl; and alkenyl radicals such as vinyl, or allyl. Methyl and phenyl are preferred for R. The subscript n is an integer with a value of zero or greater, and the subscript m is an integer from 3 to 20. The vapor pressure is too low at m greater than 20, which makes introduction into the plasma polymerization device problematic. The cyclic organosi-

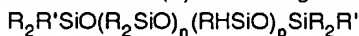
loxane under discussion is exemplified by cyclic organosiloxanes with the following formulas, in which Me hereinafter denotes methyl:



and

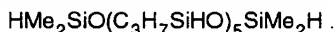
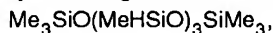


The second organosiloxane used in our invention is (B) a linear organosiloxane with the following general formula



wherein R denotes a C₁ to C₁₈ monovalent hydrocarbon radical and R' is a silicon-bonded hydrogen atom or a C₁ to C₁₈ monovalent hydrocarbon radical. R and R' are exemplified by the same radicals as given above for R of organosiloxane (A) where R' is a hydrocarbon group. The subscript n is an integer with a value of zero or greater, and p is an integer having a value of 1 to 20. The vapor pressure is too low at p greater than 20, which makes introduction into the plasma polymerization device problematic.

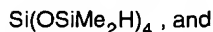
Subject linear organosiloxane is exemplified by linear organosiloxanes with the following formulas:



The third organosiloxane used by this invention is (C) an organosiloxane with the following general formula:



wherein R denotes a C₁ to C₁₈ monovalent hydrocarbon radical and is exemplified by the same radicals as given above for component (A). The subscript x is 3 or 4. This organosiloxane used in the present invention is exemplified by organosiloxanes with the following formulas.



The organosiloxanes used in the present invention are liquids at room temperature that exhibit high volatilities, and as such are easily managed, for example, for introduction in vapor form into the plasma polymerization device.

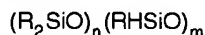
Any substrate that permits deposition of plasma-polymerized films from the SiH-containing organosiloxane described above can be used as the substrate for deposition of the water-repellent thin films of this invention, but otherwise its qualities are not crucial. The substrate is exemplified by inorganic substrates such as glasses, silica glasses, quartz, silicon wafers, ceramics, and metals of various types, and by organic substrates such as polycarbonate, polyethylene, polypropylene, and polymethyl methacrylate. The substrate may have various shapes, for example, flat sheet, a curved sheet-like surface, block-like, and so forth. Thus, the shape of the substrate is not specifically restricted with the exception that powders are excluded.

The water-repellent thin films of our invention are obtained by plasma polymerization of the SiH-containing orga-

nosiloxane described above. These films are very hard and generally have a pencil hardness of at least HB. Their water repellency corresponds to a contact angle versus water of at least 90°.

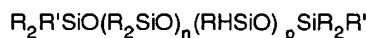
The water-repellent thin films of this invention are prepared by a method wherein an SiH-containing organosiloxane selected from the group consisting of:

(A) a cyclic organosiloxane with the general formula



wherein R denotes a C₁ to C₁₈ monovalent hydrocarbon radical, n is an integer with a value of zero or greater, and m is an integer with a value from 3 to 20,

(B) a linear organosiloxane with the general formula



wherein R denotes a C₁ to C₁₈ monovalent hydrocarbon radical, R' is a C₁ to C₁₈ monovalent hydrocarbon radical or a silicon-bonded hydrogen atom, n is an integer with a value of zero or greater, and p is an integer with a value from 1 to 20, with the proviso that this organopolysiloxane contains at least 3 silicon-bonded hydrogen atoms, and

(C) an organosiloxane with the general formula



wherein R denotes a C₁ to C₁₈ monovalent hydrocarbon radical and x is 3 or 4 is introduced into a plasma polymerization device. The SiH-containing organosiloxane is then plasma polymerized in the presence of an oxygen-containing compound selected from the group consisting of water, air, and C₁ to C₁₀ alcohols and thereby deposited on the surface of an inorganic or organic substrate, which is also present in the polymerization device.

The organosiloxane used our method is the same as the organosiloxane described above in the explanation of the water-repellent thin films. In the present invention, the described organosiloxane is introduced into a plasma polymerization device and plasma polymerized, in the presence of an oxygen-containing compound selected from the group consisting of water, air, and alcohols having 1 to 10 carbon atoms, and are thereby deposited on the surface of an inorganic or organic substrate. The organosiloxane is preferably introduced as a vapor, and this vapor is generated by heating the organosiloxane at room temperature up to, as a general rule, 200°C. The thus-generated vapor is preferably diluted with an inert carrier gas, (e.g., nitrogen, argon, helium, and so forth) or a gas such as oxygen or air and then transported to the plasma polymerization device. The C₁ to C₁₀ alcohol is exemplified by methanol, ethanol, propanol, and butanol.

In the instant method, the substrate is first placed in the plasma polymerization device and the interior of the plasma polymerization device is then evacuated. The evaporated SiH-containing organosiloxane is subsequently introduced and a plasma polymerization is induced by a glow discharge generated by electrodes installed in the plasma polymerization device. This plasma polymerization is preferably run under mild conditions to preserve the backbone structure of the SiH-containing organosiloxane to the greatest extent possible. For example, the plasma discharge is preferably run at a vacuum no greater than 1.3 kPa (10 Torr) and preferably no greater than 0.7 kPa (5 Torr) at a frequency in the range from 1 to 100 MHz and an output in the range from 1 to 100 W (Watt). The temperature is preferably held in the range from room temperature to 200°C.

The SiH-containing organosiloxane will plasma polymerize under these conditions and becomes deposits on the substrate surface. Its deposited thickness varies in almost direct proportion to increases in the plasma polymerization time and increases in the feed of vaporized organosiloxane, and these parameters are therefore used to adjust the deposited thickness.

The thickness of the water-repellent film thereby produced will vary according to its application, but these films are generally prepared in thicknesses ranging from 0.001 to 5 micrometers.

Examples

The present invention is explained in greater detail below through illustrative examples. The deposited thickness reported for the plasma-polymerized films in the examples is the value calculated from the deposition rate as determined by measurement of the film thickness using a needle contact-type film thickness meter (alpha-STEP200™ from Tokyo Electron Kabushiki Kaisha, Japan) for plasma polymerization on a glass slide under the same conditions of pressure and applied power.

Example 1

A grounded stainless steel base (diameter = 100 mm) was placed in a glass bell jar (diameter = 22 cm), and maintained at a temperature of 100°C. A power-application electrode (diameter = 80 mm) was fixed at a position 20 mm above this base. A glass slide (length = 76 mm; width = 26 mm; and thickness = 1 mm) was subsequently placed on the base and the interior of the jar was placed under a vacuum. Then, a flow of tetramethylcyclotetrasiloxane (MeHSiO_4) was set up using dry air as a carrier gas to give an internal pressure of 0.2 kPa (mbar), and a plasma polymerization was run for 20 minutes at a frequency of 13.56 MHz and an applied power of 10 W.

After completion of the plasma polymerization, the internal pressure was released to ambient pressure and the glass slide was removed. A transparent and uniform thin film had formed on the glass slide. A contact angle versus pure water of 103° was measured on the surface of the glass slide carrying the thin film. This thin film had a pencil hardness of 3H, as measured by the method of JIS K 5400, "The Pencil Scratch Test for Coatings." The plasma-polymerized film had a deposited thickness of 100 nm.

Example 2

A grounded stainless steel base (diameter = 100 mm) was placed in a glass bell jar (diameter = 22 cm) and maintained at a temperature of 60 °C. A power-application electrode (diameter = 80 mm) was fixed at a position 20 mm above this base. A glass slide was subsequently placed on the base and the interior of the jar was placed under a vacuum. Then, a flow of the linear organosiloxane $\text{Me}_2\text{HSiO}(\text{MeHSiO})_2\text{SiMe}_2\text{H}$ was set up using dry air as a carrier gas to give an internal pressure of 0.3 kPa (mbar), and a plasma polymerization was run as in Example 1 for 20 minutes at an applied power of 25 W.

After completion of the plasma polymerization, the internal pressure was released to ambient pressure and the glass slide was removed. A transparent and uniform thin film had formed on the glass slide. A contact angle versus pure water of 100° was measured on the surface of the glass slide carrying the thin film. This thin film had a pencil hardness of 4H, as measured by the method of JIS K 5400. The plasma-polymerized film had a deposited thickness of 200 nm.

Example 3

A grounded stainless steel base (diameter = 100 mm) was placed in a glass bell jar (diameter = 22 cm), and maintained at a temperature of 60 °C. A power-application electrode (diameter = 80 mm) was fixed at a position 20 mm above this base. A silicon wafer (2 cm²) was subsequently placed on the base and the interior of the jar was placed under a vacuum. Then, a flow of the organosiloxane $\text{MeSi}(\text{OSiMe}_2\text{H})_3$ was set up using dry air as a carrier gas to give an internal pressure of 0.2 kPa (mbar), and a plasma polymerization was run as in Example 1 for 15 minutes at an applied power of 10 W.

After completion of the plasma polymerization, the internal pressure was released to ambient pressure and the silicon wafer was removed. A transparent and uniform thin film had formed on the silicon wafer. A contact angle versus pure water of 98° was measured on the surface of the silicon wafer carrying the thin film. The plasma-polymerized film had a deposited thickness of 150 nm.

Comparative Example 1

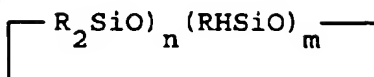
A plasma polymerization was run as in Example 2, but in this case using the linear organosiloxane $\text{Me}_3\text{Si}(\text{MeHSiO})_2\text{SiMe}_3$ in place of the linear organosiloxane $\text{Me}_2\text{HSiO}(\text{MeHSiO})_2\text{SiMe}_2\text{H}$ that was used in Example 2.

The resulting thin film was soft, having a pencil hardness no greater than B, and could not be used as a water-repellent thin film.

Claims

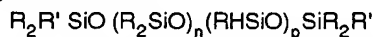
1. A water-repellent thin film, obtained by plasma polymerizing an SiH-containing organosiloxane on a substrate, said organosiloxane being selected from the group consisting of

(A) a cyclic organosiloxane of the general formula



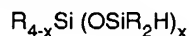
wherein R denotes a monovalent hydrocarbon radical having 1 to 18 carbon atoms, n is an integer having a value of zero or greater and m is an integer having a value of 3 to 20;

(B) a linear organosiloxane of the general formula



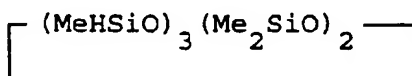
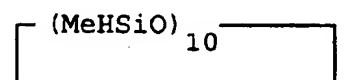
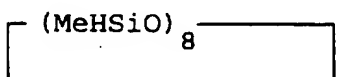
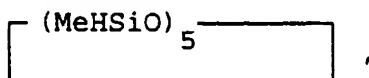
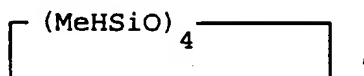
wherein R and n are as defined above, R' is selected from a monovalent hydrocarbon radical having 1 to 18 carbon atoms or a silicon-bonded hydrogen atom and p is an integer having a value of 1 to 20, with the proviso that organosiloxane (B) contains at least 3 silicon-bonded hydrogen atoms; and

(C) an organosiloxane compound with the general formula

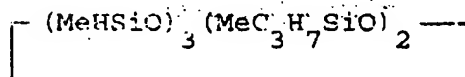


wherein R is as defined above and x is 3 or 4.

2. The film according to claim 1, wherein said film has a pencil hardness of at least HB and a contact angle versus water of at least 90°.
3. The film according to claim 2, wherein said cyclic organosiloxane (A) has a formula selected from the group consisting of



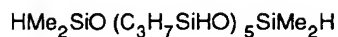
and



in which Me denotes methyl.

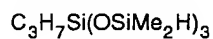
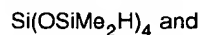
4. The film according to claim 2, wherein said linear organosiloxane (B) has a formula selected from the group consisting of





in which Me denotes methyl.

- 5 5. The film according to claim 2, wherein said organosiloxane compound (C) has a formula selected from the group consisting of



10 in which Me denotes methyl.

6. A method for preparing a water-repellent thin film, said method comprising plasma polymerizing the SiH-containing organosiloxane of claim 1 in a plasma polymerization device in the presence of a substrate and in the presence of an oxygen-containing compound selected from the group consisting of water, air and an alcohol having 1 to 10 carbon atoms.

7. A substrate bearing a film deposited by the method of any of claims 1 to 6 wherein said substrate is selected from the group consisting of glass, quartz, silicon, ceramic, metal, polycarbonate, polyethylene, polypropylene and polymethyl methacrylate.

